

# Characterization of the efficiency of antiscaling treatments of water. Part II: Physical processes

A. KHALIL<sup>1,2</sup>, R. ROSSET<sup>2</sup>, C. GABRIELLI<sup>1\*</sup>, M. KEDDAM<sup>1</sup>, H. PERROT<sup>1</sup>

<sup>1</sup>Laboratoire de Physique des Liquides et Électrochimie UPR 15 CNRS – Tour 22, 4 Place Jussieu, 75252 Paris, Cedex 05, France; <sup>2</sup>Laboratoire de Chimie Analytique des processus Industriels URA CNRS no. 437 Paris, France

(\*author for correspondence, e-mail: cg@ccr.jussieu.fr)

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The efficiency of physical antiscaling treatments of water was evaluated by various techniques, such as chronoamperometry, electrochemical impedance and chronoelectrogravimetry. It was found that the antiscaling electrolytic treatment is more efficient than magnetic treatment, at least for the commercial devices used here, and that it also has a longer lasting effect. The electrolytic process generates  $\text{CaCO}_3$  nuclei in suspension in the bulk water, which provokes homogeneous scaling rather than heterogeneous scaling on the walls which is to be avoided. If the small crystals generated in the bulk are eliminated by filtration, surface scaling is again observed.

Keywords: antiscaling, treatment, electrolytic,  $\text{CaCO}_3$

## 1. Introduction

Many antiscaling physical treatments of natural waters have been proposed [1]. These are based on four different physical principles: water electrolysis, high frequency electromagnetic waves, permanent magnets and ultrasonic waves.

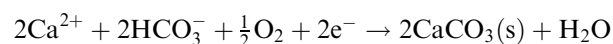
Although few scientific papers have been published, many patents (more than 100 between 1966 and 1988 with an increase in the last few years) have been registered. Recently, numerous commercial devices have appeared on the market offering antiscaling treatment [2]. The commercial notes generally offer similar advantages for the treatment: namely, (i) the processes have low energy cost; (ii) the processes are independent of the nature of the water to be treated; (iii) the chemical composition of the water is not changed and its potability is not affected; and (iv) the processes are not only preventative but curative (i.e., when the pipes or the devices are previously scaled it is claimed that, after treatment, the scale decays and is eliminated, being carried away by the treated water flow).

This investigation concerns the efficiency of antiscaling devices based on electrolytic and magnetic processes evaluated by techniques described in the previous paper dealing with the chemical processes [3–7].

## 2. Electrolytic process

Some antiscaling treatments are based on water electrolysis [8–10]. The present device, has been commercialized under the trademark EAUTONIC (from CRIS, Technique de l'Eau). It consists of a cylindrical tank (140 mm diam., 250 mm height) and a control

system which generates an electrical signal between a titanium electrode and the stainless steel tank which is cathodically polarized. The water flows in the electrolysis tank from bottom to top. The electrical signal is an a.c. voltage (0 to 10 V and 1 Hz to 1 MHz) superimposed on a d.c. voltage (0 to 10 V). The d.c. voltage allows the scale to be deposited on the cathodically polarized walls of the tank, whereas the a.c. voltage impedes the scale from encrusting the walls. This favours bulk  $\text{CaCO}_3$  formation by homogeneous nucleation through the electrochemical reaction:



from where it is carried away by the water flow.

### 2.1. Efficiency estimation

Natural water with a calcium concentration of  $100 \text{ mg dm}^{-3}$  was passed through the electrolytic tank at a low flow rate ( $10 \text{ dm}^3 \text{ h}^{-1}$ ). Figure 1 shows chronoelectrogravimetric curves obtained with an immersed jet cell for an approximately 3.5 h test. For nontreated water (curve 1) the nucleation time is 40 min and the scaling rate is  $0.4 \mu\text{g cm}^{-2} \text{ s}^{-1}$ . For treated water, the nucleation time is practically infinite and the scaling rate is zero. After treatment, measurement of  $\text{Ca}^{2+}$  concentration demonstrated a decrease to  $16 \text{ mg dm}^{-3}$ . Therefore,  $\text{CaCO}_3$  was precipitated either in the bulk or on the tank walls. However, as the current did not change during the test,  $\text{CaCO}_3$  was formed in the bulk solution.

The electrode impedance was measured during accelerated scaling for untreated and treated waters. Impedance diagrams are plotted in Fig. 2. In Table 1,

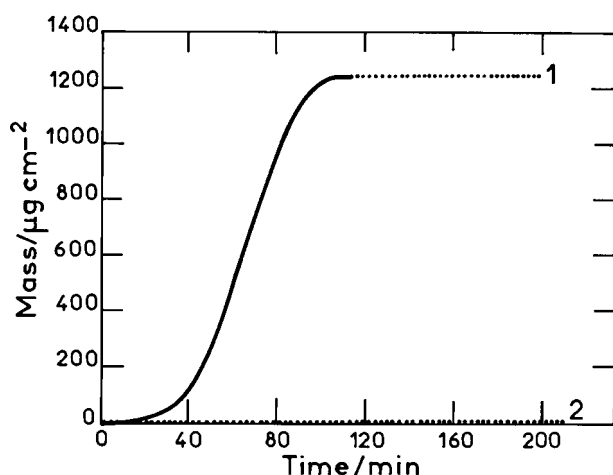


Fig. 1. Chronoelectrogravimetric curves plotted for a natural water: untreated (1) and treated (2) through an electrolytic process.

Table 1. Experimental parameters deduced from the impedances diagrams of Fig. 2 measured for an electrolytic treatment

Water	Measurement after	$R_e$ / $\Omega$	$R_{HF}$ / $\Omega$ cm <sup>2</sup>	$R_d$ / $\Omega$ cm <sup>2</sup>	$C_{HF}$ / $\mu$ F
Non-treated water	10 min	410	300	1140	10
	1 h	400	800	2580	10
	2 h	400	7500	3780	0.2
Treated water	10 min	500	670	650	50
	1 h	580	660	670	30
	2 h	570	500	600	20

the quantities  $R_{HF}$  and  $C_{HF}$ , deduced from the high frequency loop, are given. For treated water these parameters changed very little with time up to 2 h.

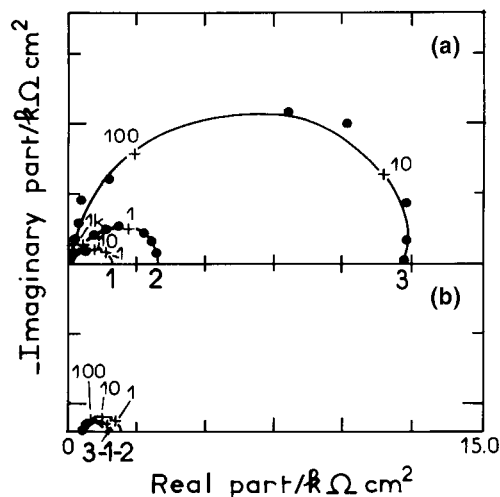


Fig. 2. Measured electrochemical impedances for a natural water: untreated (a) and treated (b) by an electrolytic process after (1) 10 min, (2) 1 h and (3) 2 h of scale deposition.

For untreated water, large changes occurred, from 300  $\Omega$  cm<sup>2</sup> at the beginning to 7500  $\Omega$  cm<sup>2</sup> after 2 h.  $C_{HF}$  was divided by 50 whereas it was only divided by 2.5 for treated water. This shows that the blocking rate is much less significant for treated water.

A 25% increase in the electrolyte resistance was observed after water treatment. This was probably due to formation of  $\text{CaCO}_3$  nuclei in the bulk solution, which is in agreement with the decrease in the  $\text{Ca}^{2+}$  concentration, leading to a more resistant water.

The electrode surface was observed using a scanning electron microscopy (SEM) (Figs. 3 and 4). These observations were in agreement with electrogravimetry: whichever the considered stages (10 min,

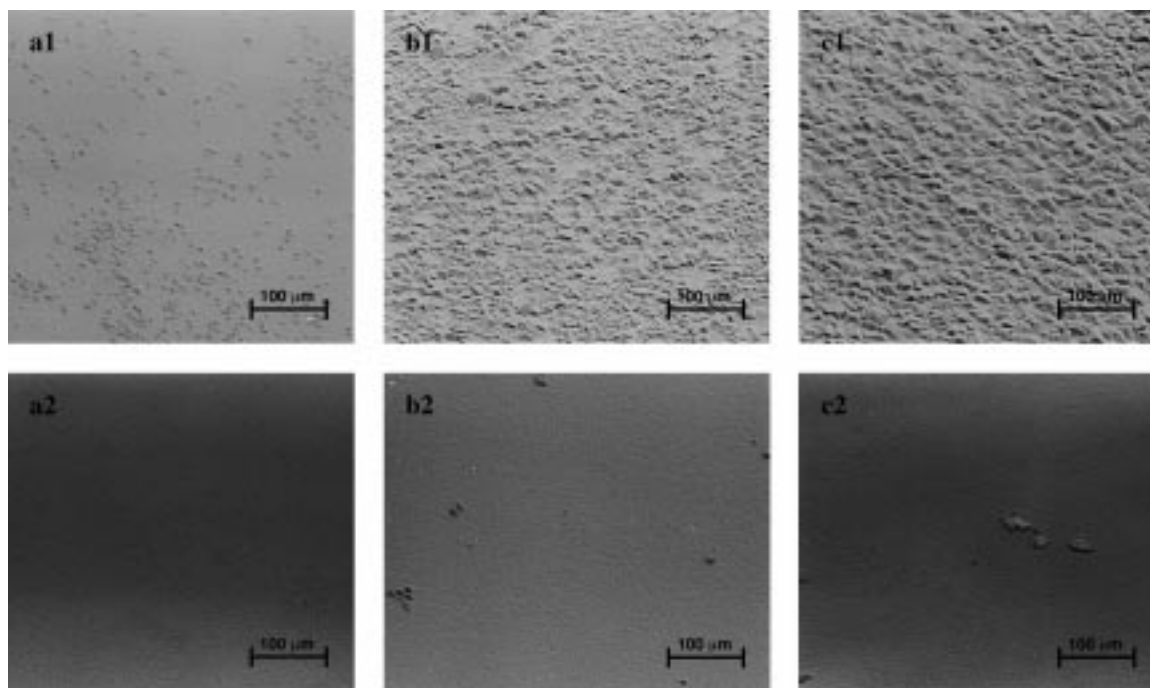


Fig. 3. Observation of the electrode surface by SEM: for untreated water after (a1) 10 min, (b1) 1 h and (c1) 2 h; and treated water after (a2) 10 min, (b2) 1 h and (c2) 2 h deposition.

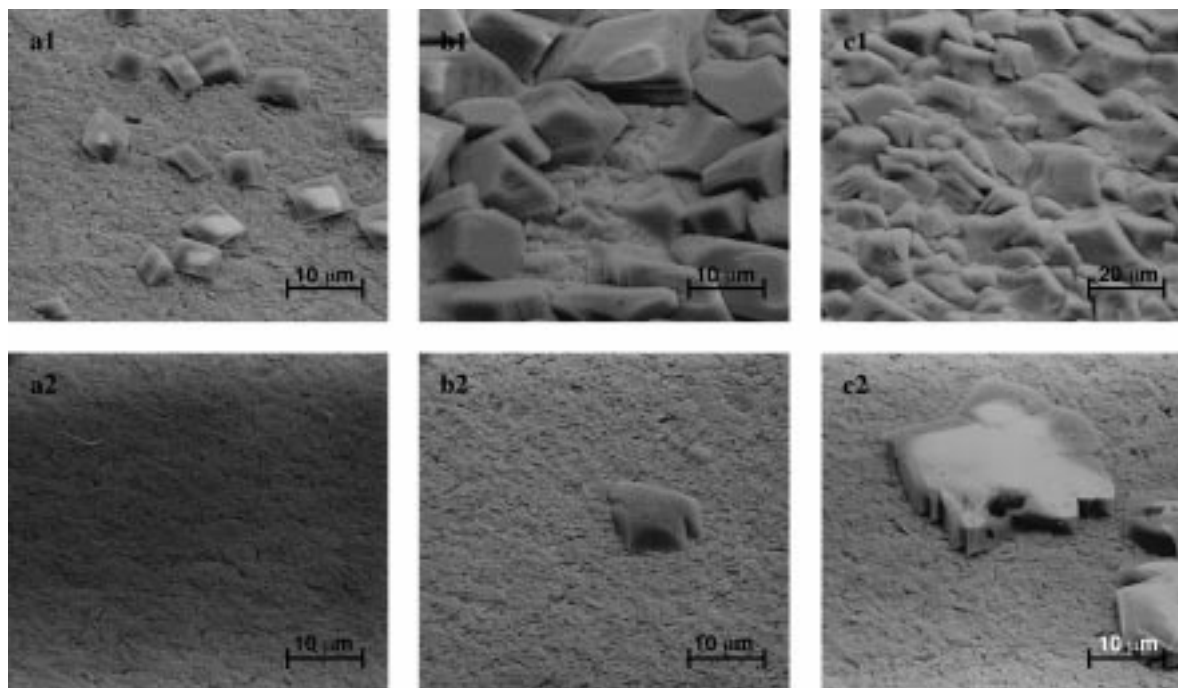


Fig. 4. As for Fig. 3. with higher magnification.

1 h, 2 h) the scale coverage was insignificant for treated water, whereas it was total for untreated water. However, a limited number of badly crystallised  $\text{CaCO}_3$  aggregates were observed for treated water. Therefore, the electrolytic process modifies both the kinetics and the morphology of  $\text{CaCO}_3$  scaling.

## 2.2. Remanence of the electrolytic process

It was shown that the electrolytic process was quite efficient when electrogravimetry was carried out just after the treatment (Fig. 1). However, in contrast to chemical processes, where the antiscaling reagents remain in the treated water, physical treatment is effective only for a relatively short time and then vanishes as the water flows through the treatment device. In spite of this, Fig. 5 shows that, even after

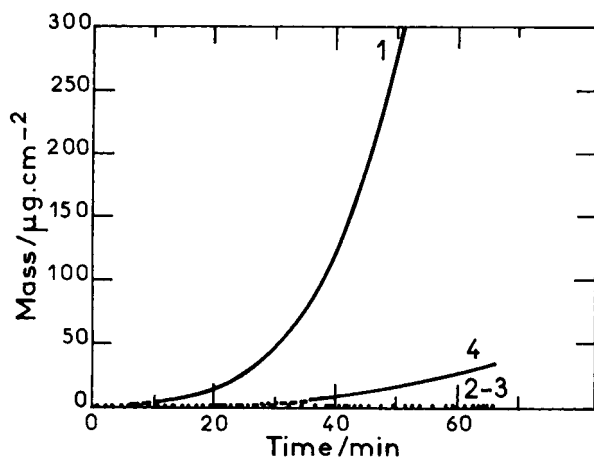


Fig. 5. Remanence of the electrolytic process studied by chronoelectrogravimetry. (1) Untreated water, (2) just after treatment, (3) treated water stored 5 h and (4) treated water stored 48 h.

5 h storage, the efficiency is not changed; beyond and up to 48 h storage, the efficiency decreased but remained significant.

## 2.3. Filtration of the treated water

Water treated by the electrolytic process was filtered through a  $0.45 \mu\text{m}$  filter (Millex, Millipore) and then analyzed by chronoelectrogravimetry.

Figure 6 shows a comparison of the chronoelectrogravimetric curves obtained for filtered, nonfil-

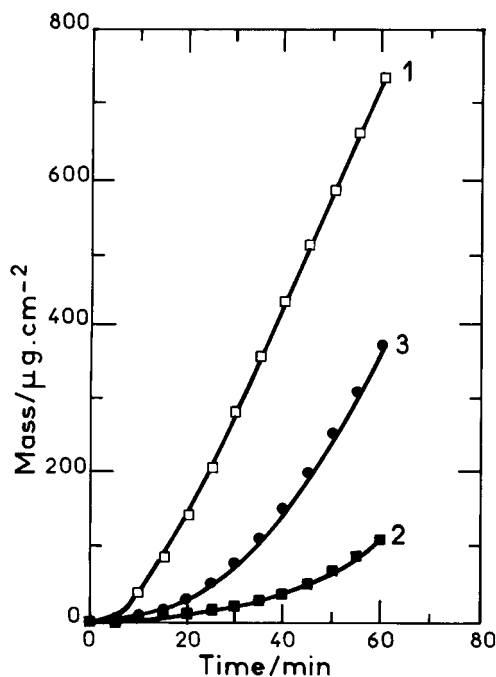


Fig. 6. Chronoelectrogravimetric curves of untreated and filtered treated water. (1) Nontreated water, (2) nonfiltered treated water and (3) filtered treated water.

tered treated water and nontreated water. For filtered treated water the amount of deposited  $\text{CaCO}_3$  is larger at a given time (curve 3) than for nonfiltered treated water (curve 2). Therefore, removal of the  $\text{CaCO}_3$  clusters from the treated water increased its heterogeneous scaling power.

The particles which were collected in the filters were observed by SEM and then analysed by X-ray spectroscopy (Fig. 7). For a nontreated water, no  $\text{CaCO}_3$  particles were identified; this was confirmed by X-ray spectroscopy where no calcium peak was detected. A peak corresponding to the gold previously evaporated for SEM examination and another peak for Si which was an impurity of the water were observed. For treated water badly crystallized globular clusters of  $\text{CaCO}_3$  were found. This was clearly confirmed by X-ray spectroscopy where the Ca peak is very high.

Therefore, the electrolytic process produces badly crystallized  $\text{CaCO}_3$  nuclei in the water bulk. As these nuclei do not form a deposit on the tank walls, the scaling power of the water decreases. However, if these nuclei are eliminated by filtration, scaling properties of the filtered water became close to those of nontreated water.

#### 2.4. Particle counting

Optical counters allow the determination of the particle size and number in water down to  $1\ \mu\text{m}$  (mea-

surement of particle size down to  $0.1\ \mu\text{m}$  would need laser detection counters). The technique is based on the measurement of the quantity of light attenuated by the particles in suspension in the analysed water which is directly proportional to the accumulated surface of the particles.

In nontreated water many kinds of particle were already in suspension: microorganisms, mud, pipe fragments, corrosion products and colloids. Then particle counting in nontreated water already showed a great number of particles (Fig. 8(a)). However, counting revealed a significant increase in the number of diluted particles in treated water (Fig. 8(b)). This increase is due to the formation of  $\text{CaCO}_3$  nuclei in bulk solution. After a 24 h rest a new count showed that the number of particles drastically diminished for all sizes considered for treated and untreated water. During this 24 h rest period all the particles tended to precipitate, the  $\text{CaCO}_3$  particles generated by electrolysis seemed to have less tendency to form a precipitate which explains that the decrease was less significant for treated than for untreated waters. The  $\text{CaCO}_3$  particles generated having the same charge, might repel and coalesce less easily than those in suspension in untreated water.

#### 3. Magnetic treatment

Magnetic treatments have been used for antiscaling purposes [11–16]. A commercial device (SAFOG,

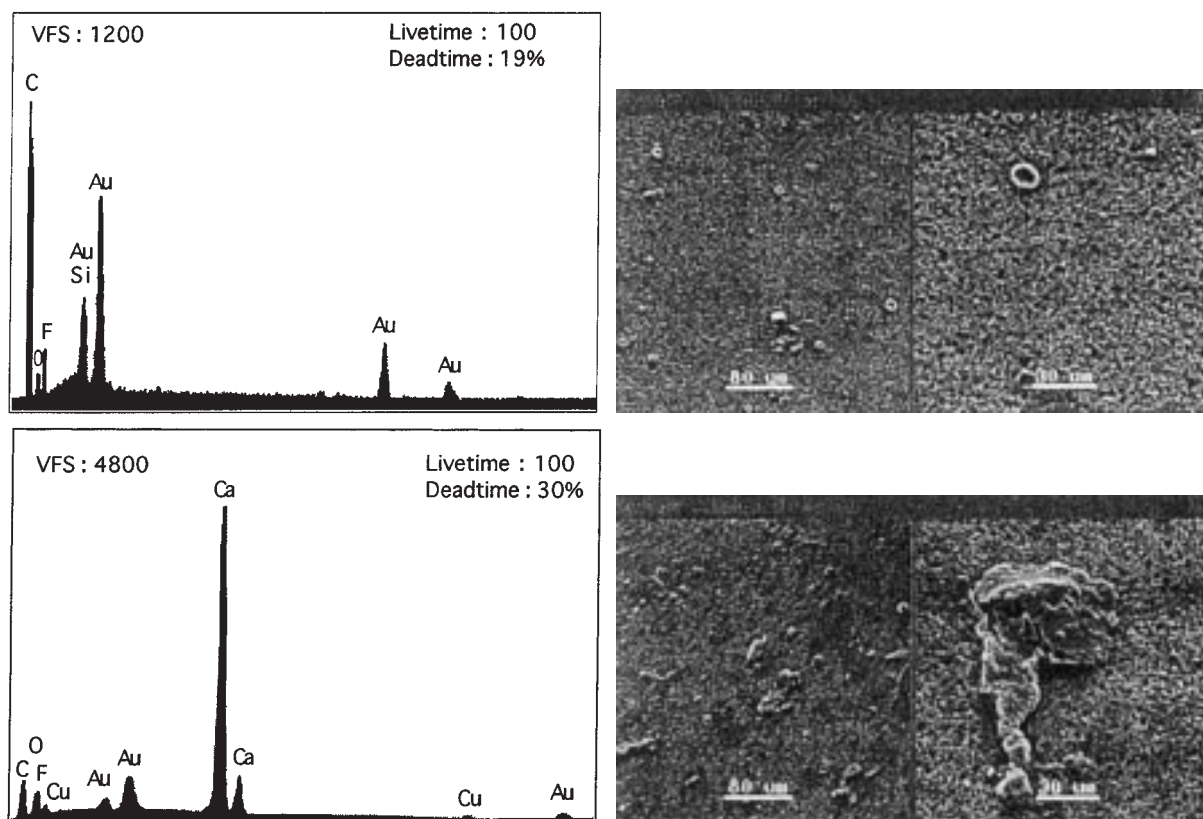


Fig. 7. (a) SEM X-ray spectroscopy and observation of the solid obtained from filtration of untreated water. (b) SEM X-ray spectroscopy and observation of the solid obtained from filtration of treated water.

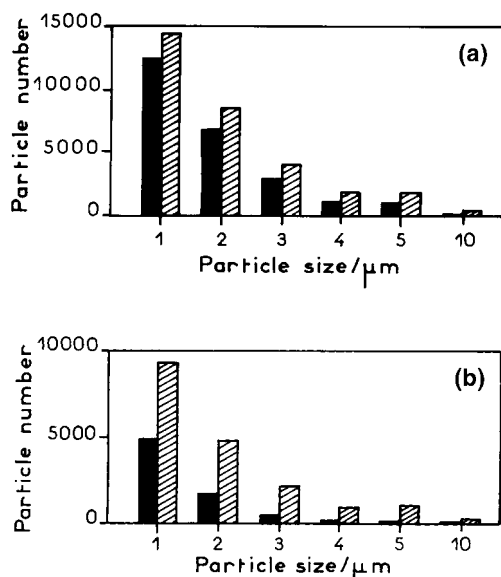


Fig. 8. Particle counting on untreated water and treated water (a) just after treatment and (b) after a 24 h storage.

manufactured by A.M.I. Fluid, Montpellier, France) based on a magnetic treatment was tested. The water passed through a pipe (50 cm long  $\times$  12 cm diam.) enclosed in an ensemble of 14 magnets with inversed polarity having a 1.26 T remanent induction. The magnets were arranged alternatively on two planes intersecting at  $60^\circ$  in order that all the odd magnets are located on the first plane and the even magnets on the second plane. At the top, the north pole of all the odd magnets and the south pole of the even magnets, were positioned. The flow rate was usually  $2 \text{ m}^3 \text{ h}^{-1}$ .

### 3.1. Efficiency estimation

Figure 9 shows a large increase of the nucleation time when water was treated magnetically. This quantity increased from 30 min for nontreated water to 70 min for treated water. Similarly, the scaling time was greater by a factor two for treated water. However, the scaling rate was very similar for nontreated and for treated waters. A good reproducibility of the experiments carried out on different days was found.

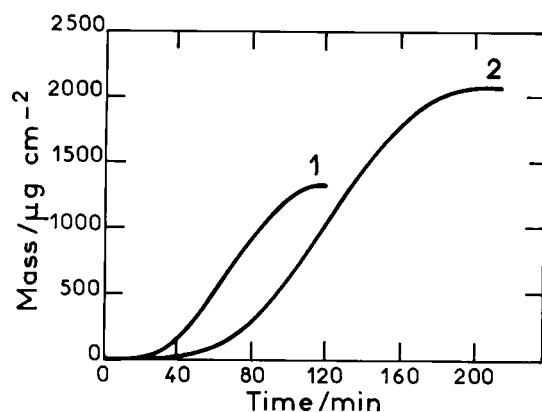


Fig. 9. Chronoelectrogravimetric curves for (1) nontreated and (2) treated waters with a magnetic process.

As for the electrolytic process the change in the electrode impedance was followed for treated and nontreated waters during  $\text{CaCO}_3$  deposition. Figure 10 shows the impedance diagrams plotted after 10 min, 1 h and 2 h of scaling. The experimental quantities deduced from the impedance are gathered in Table 2. The analysis of these parameters allows the change of  $R_{\text{HF}}$ ,  $C_{\text{HF}}$  and  $R_d$  to be followed. They showed that after 10 min, or even 1 h, no difference was observed by impedance between treated and nontreated waters, although electrogravimetry measurements already showed significant differences.

However after 2 h, the impedance measured in nontreated water demonstrated a blocked electrode behaviour.  $R_{\text{HF}}$  was equal to  $7700 \Omega \text{ cm}^2$  whereas it was only  $380 \Omega \text{ cm}^2$  after 1 h.  $C_{\text{HF}}$  changed from  $20 \mu\text{F}$  to  $0.5 \mu\text{F}$  which showed a complete coverage of the electrode by  $\text{CaCO}_3$  scale. These results are in agreement with electrogravimetry.

Scanning electron microscope observations were performed at various deposition times (Figs. 11 and 12). For nontreated water, after 10 min, some  $5 \mu\text{m}$   $\text{CaCO}_3$  nuclei were already uniformly distributed on the electrode surface. After 1 h they had grown and  $20 \mu\text{m}$  crystals were observable, but no other nuclei appeared. This observation shows that the active surface (which is not covered by  $\text{CaCO}_3$ ) was not

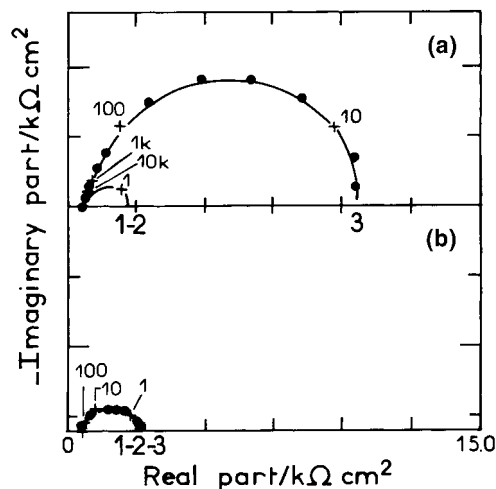


Fig. 10. Measured electrochemical impedances for a natural untreated water (A) and treated water (B) by a magnetic process after (1) 10 min, (2) 1 h and (3) 2 h of scale deposition.

Table 2. Experimental parameters deduced from the impedance diagrams of Fig. 9 measured for a magnetic treatment

Water	Measurement after	$R_e / \Omega$	$R_{\text{HF}} / \Omega \text{ cm}^2$	$R_d / \Omega \text{ cm}^2$	$C_{\text{HF}} / \mu\text{F}$
Non-treated water	10 min	500	270	930	17
	1 h	560	380	400	21
	2 h	540	7740	1705	0.5
Treated water	10 min	600	480	700	18
	1 h	510	490	740	19
	2 h	540	1400	770	15

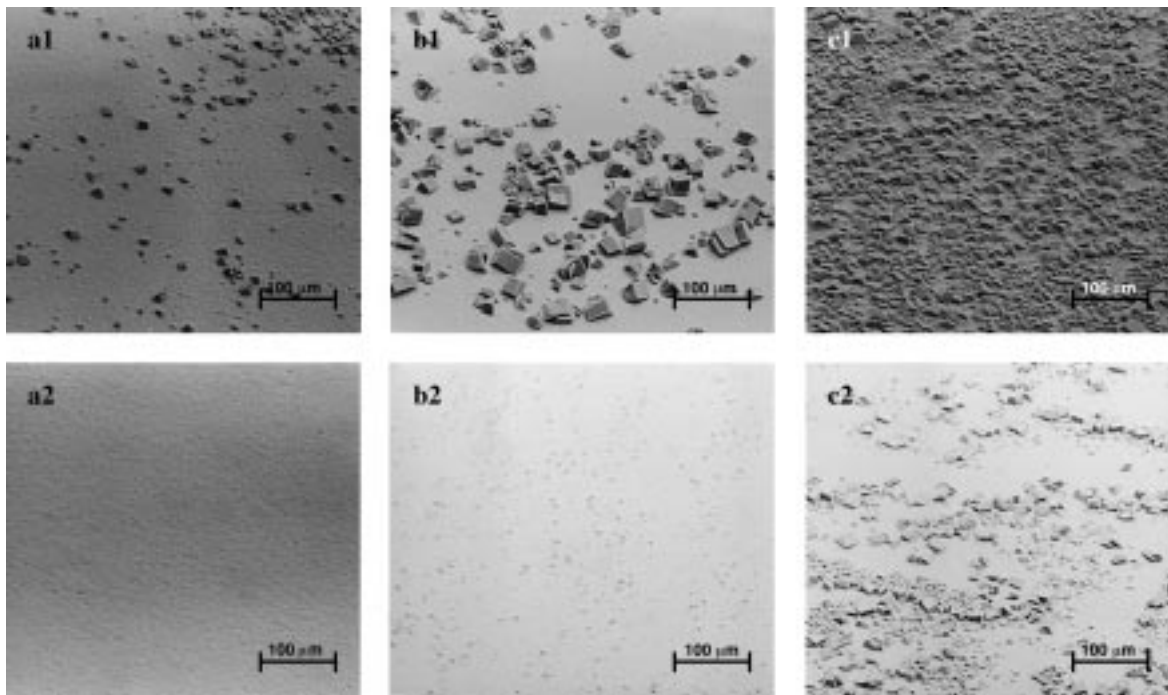


Fig. 11. Observation of the electrode surface by means of a SEM for untreated water after (a1) 10 min; (b1) 1 h; (c1) 2 h and treated water after (a2) 10 min; (b2) 1 h; (c2) 2 h deposition.

changed. This confirms the results obtained by impedance measurement and electrogravimetry. After 2 h the electrode was entirely covered. All the crystals already visible after 1 h were always about  $20\ \mu\text{m}$  in size but between them a porous layer of smaller crystals of about  $10\ \mu\text{m}$  was inserted.

For treated water, after 10 min, no  $\text{CaCO}_3$  nuclei was visible. However with a higher magnification

minute nuclei,  $2\ \mu\text{m}$  in size, were observable. X-ray spectroscopy of these clusters allowed  $\text{CaCO}_3$  to be identified (Fig. 13). After 1 h, small clusters were observable but they had a size four times lower than for the nontreated water. After 2 h, only a growth of the  $\text{CaCO}_3$  clusters was observed. The active surface remained significant whereas it practically disappeared for nontreated water. This result was in

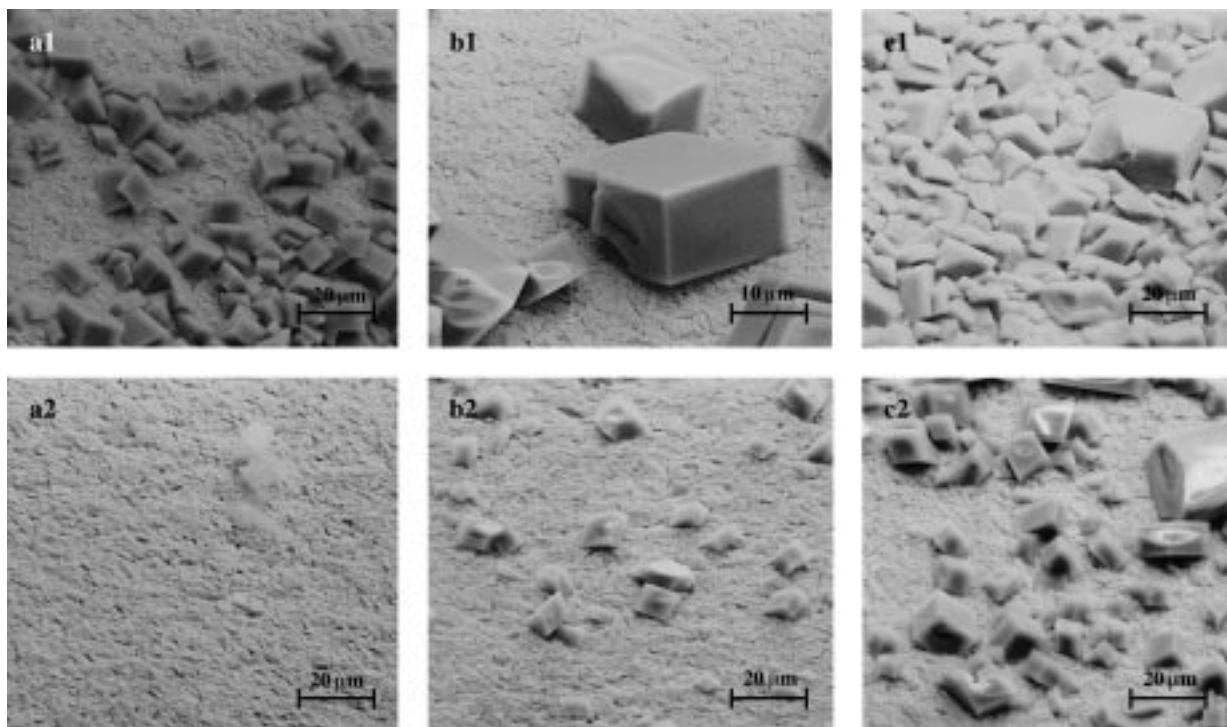


Fig. 12. As for Fig. 11 with higher magnification.

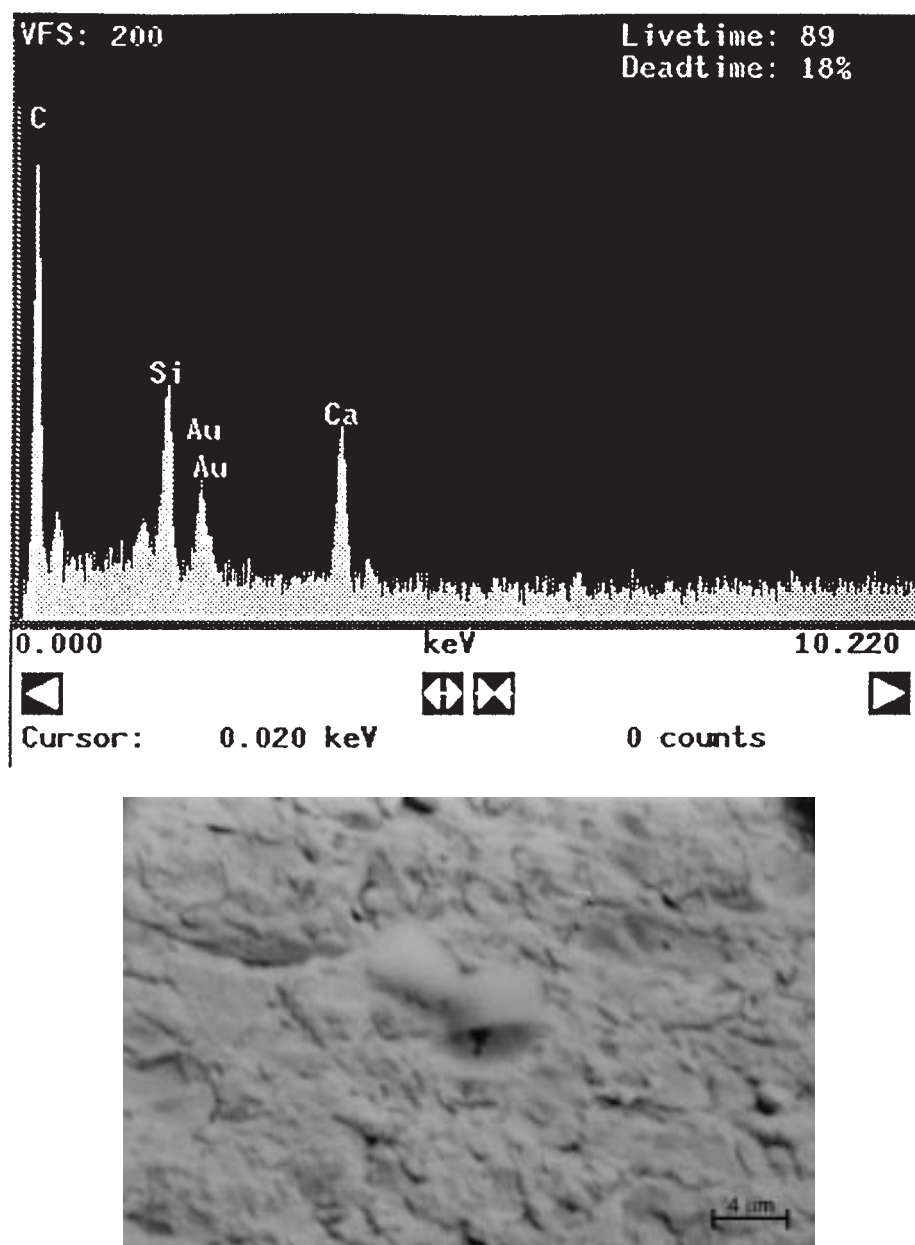


Fig. 13. SEM observation and X-ray spectroscopy of a small nuclei after 10 min  $\text{CaCO}_3$  deposition from a water treated by a magnetic process.

agreement with impedance measurement, after 2 h of deposition, where  $C_{\text{HF}}$  was 30 times greater in treated water than in nontreated water.

### 3.2. Influence of the flow rate

Figure 14 shows the  $\text{CaCO}_3$  mass deposited with time for various flow rates and comparison with nontreated water. These chronoelectrogravimetric curves show that the scaling rate decreased when the flow rate increased. For  $1.2 \text{ m}^3 \text{ h}^{-1}$  flow rate of the water passing through a magnetic device, the  $\text{CaCO}_3$  deposited mass was twice less important.

### 3.3. Remanence of the magnetic treatment

After 2 h storage the efficiency of the magnetic treatment remained significant. In contrast, if the

treated water was stored for 5 h, the  $\text{CaCO}_3$  mass deposited became five times greater after 1 h scaling compared to treated but nonstored water (Fig. 15).

## 4. Conclusion

The results obtained by various techniques (chronamperometry, impedance and chronoelectrogravimetry) are in agreement for the efficiency evaluation of physical antiscaling treatment of waters. The antiscaling electrolytic treatment is more efficient than the magnetic treatment (at least for the commercial devices used here). In addition the magnetic process has a lower permanence than the electrolytic process.

Concerning the action of the antiscaling treatment on nucleation, it seems that the electrolytic process generates  $\text{CaCO}_3$  nuclei in suspension in the bulk water, which provokes homogeneous scaling in the



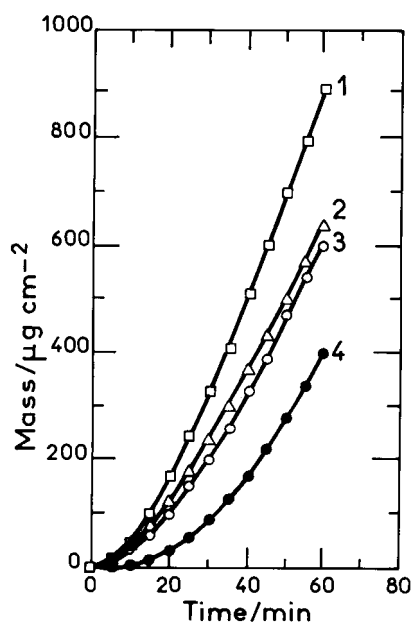


Fig. 14. Influence of the flow rate on the chrono-electrogravimetric curves obtained on water treated by the magnetic process. (1) nontreated water, (2)  $200 \text{ dm}^3 \text{ h}^{-1}$  treated water, (3)  $600 \text{ dm}^3 \text{ h}^{-1}$  treated water and (4)  $1200 \text{ dm}^3 \text{ h}^{-1}$  treated water.

bulk water rather than heterogeneous scaling on the walls. If the small crystals generated in the bulk are eliminated by filtration, surface scaling is observed again. If the magnetic process is based on the same principle, the weak permanence would show that  $\text{CaCO}_3$  bulk nuclei redissolution would be easier in this case than for the electrolytic process.

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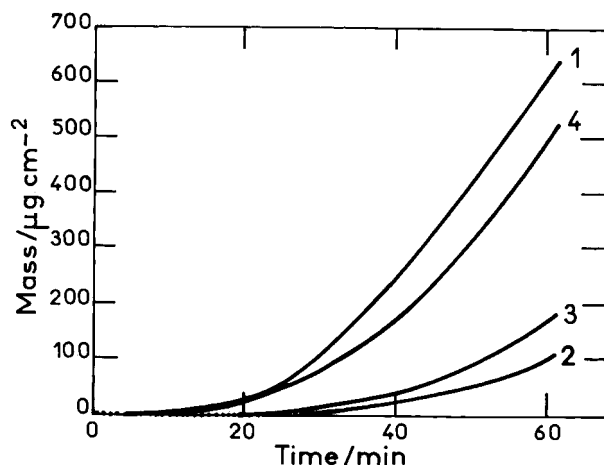


Fig. 15. Remanence of the magnetic process: chrono-electrogravimetric curves on (1) nontreated water, (2) treated but nonstored water, (3) treated water stored 2 h and (4) treated water stored 5 h.